

# **CO<sub>2</sub> Separation from Flue Gas: Evaluation of a Solid Sorbent Based Process**

<sup>1</sup>E. Gambarotta, <sup>1</sup>V. Meda, <sup>1</sup>A. Tortorella, <sup>2</sup>P. Zappelli \*

<sup>1</sup>EniTecnologie – Via F. Maritano 26 – S. Donato Milanese (MI) Italy

<sup>2</sup>EniTecnologie – Via E. Ramarini 32 – Monterotondo (RM) Italy

P. Zappelli \* - Phone: +39.06.90673.266; Fax: +39.06.90673.296

E-Mail: pzappelli@enitecnologie.eni.it

## **ABSTRACT**

*A large number of solid sorbents was prepared by impregnation of high surface, high pore volume alumina based solid supports with suitable amines. Absorption experiments were performed with a synthetic flue gas (3.4% CO<sub>2</sub>) at room temperature and the desorption was obtained by heating the sorbent at 60-100°C. The reversible CO<sub>2</sub> uptake of the best sorbents was in the range 6.5-9.5 % of the sorbent weight.*

*Based on laboratory results, the chemical and physical properties of a sorbent material, suitable for industrial applications, were assumed, which enabled us to elaborate a preliminary process design. The removal of 90% of CO<sub>2</sub> from the flue gas of a 465 MW power station was taken as a case study. An economic evaluation of the process was then performed. The CO<sub>2</sub> removal cost, as well as the CO<sub>2</sub> avoided cost were evaluated, and compared with the performance of a conventional liquid amine process.*

*The results of the evaluation show that the solid sorbent process could potentially compete with the conventional one, but further improvements of the properties of the material are needed.*

## **INTRODUCTION**

The yearly worldwide CO<sub>2</sub> emission in the atmosphere of about 25 Gt, due to the use of fossil fuels is arising a growing concern for its negative climatic influence. Fossil fuels provide for 85 % of the world-wide energetic needs, and no alternative energetic sources have the potential for a notable substitute in the next future. Among the different options under examination, the one considering capture and sequestration of CO<sub>2</sub> originated by point sources, like power plants and refineries, is gaining increasing interest. Such an approach could allow for the pursuance of fossil fuel utilisation without the feared drawback of dramatic climatic changes. Key issue of the approach is the identification of new efficient and convenient technologies for the capture of CO<sub>2</sub>. Among the technologies available today [1,2], the ones based on liquid amine solutions, are the most developed, although considered far too expensive for large scale applications. Purpose of our work was the realisation of amine containing solid sorbents, for the effective and reversible capture of CO<sub>2</sub> [3,4]. Solid sorbents [5-8], as compared to the liquid counterparts, have some potential advantages such as a more efficient absorption capacity (high surface compounds allow for a high capture density), a lower energetic need in the desorption step (amine-CO<sub>2</sub> reaction compounds are surface distributed, with easy reach by fluids and heat), and a reduced environmental impact (no loss of amine to the atmosphere during the stripping step).

## **PREPARATION OF THE SORBENTS**

The new materials were obtained by the impregnation of high-surface area, high-pore volume solid supports with suitable amino compounds.

The materials considered in the present study as solid supports, come from a selection performed from a large number of experimental compounds not commercially available (silica, silica-zirconia, alumina and clay) chosen on the basis of their structural properties, such as surface area and porosimetry features. The preparation, characterisation, and CO<sub>2</sub> capture performance of all the materials of the above screening study have been reported elsewhere [4]. In this paper only a selected number of alumina based sorbents is dealt with.

The alumina supports (A1-A4) are characterised by narrow surface area (200-265 m<sup>2</sup>/g) and pore volume (0.7-1.1 ml/g) ranges.

The selected commercially available amines (N1-N5) belong to the class of alkanolamines.

TABLE 1: SORBENT COMPONENTS

Alumina Support Code	Surface Area (m <sup>2</sup> /g)	Pore volume (ml/g)	Pore Diameter ( ? )
A1	230	1.1	105
A2	200-250	0.5-0.65	75
A3	265	0.81	125
A4	200	0.70	95

Amine Code	Amine
N1	Diethanolamine (DEA)
N2	2-(2-Aminoethoxy)ethanol (AEE)
N3	N,N'-bis(2-hydroxyethyl)ethylenediamine (BIEEDA)
N4	3-methylamino-1,2-propandiol (MAPD)
N5	1-(2-Hydroxyethyl)piperazine (IEP)
N1+N3	(DEA+BIEEDA 1:1)

The general method of the sorbents preparation was as follows:

- ✍ Washing of the support with methanol and drying under vacuum (90°C/20 mmHg)
- ✍ Mixing the solid support with an equivalent weight of amine dissolved in methanol
- ✍ Gentle stirring of the suspension, 1 hour at 50°C
- ✍ Evaporating the solvent under vacuum
- ✍ Drying of the solid residue at 90°C under vacuum
- ✍ Additional washing with methanol, followed by repeated drying, if needed.

The results of the impregnation procedures and of the CO<sub>2</sub> capture tests are reported in Table 2. The alkanolamines (N) loading (expressed as the amine weight fraction of the final sorbent) was from 24.1 to 49.8 %.

### CO<sub>2</sub> absorption/desorption experiments

Testing of the CO<sub>2</sub> capture performance featured by the sorbents was executed both on a lab scale apparatus and by a thermogravimetric analysis. The experimental apparatus and operative conditions utilised have been described elsewhere [4]. The alumina based DEA sorbents showed a direct relationship between amine loading and CO<sub>2</sub> trapping, with the highest amine loading shown by Sorb-09 (47.5 %) corresponding to the highest CO<sub>2</sub> uptake (8.7 %). On the basis of these observations, the alumina support A1 was selected as the starting material for the experiments with different amine types. The impregnation of support A1 with alkanolamines (N2-N5) originated the corresponding sorbents with the CO<sub>2</sub> capture performance reported in Table 2. The alkanolamine-based sorbents gave fair results, with the best performance exhibited by Sorb-49, where a mixture of amines (N1+N3) was used. In the course of the above screening it was pointed out that the maximum capture performance by a given sorbent is not the only evaluation criterion, being other aspects, such as stability of the amino compound on the support, temperature and ease of CO<sub>2</sub> desorption, important points to be considered.

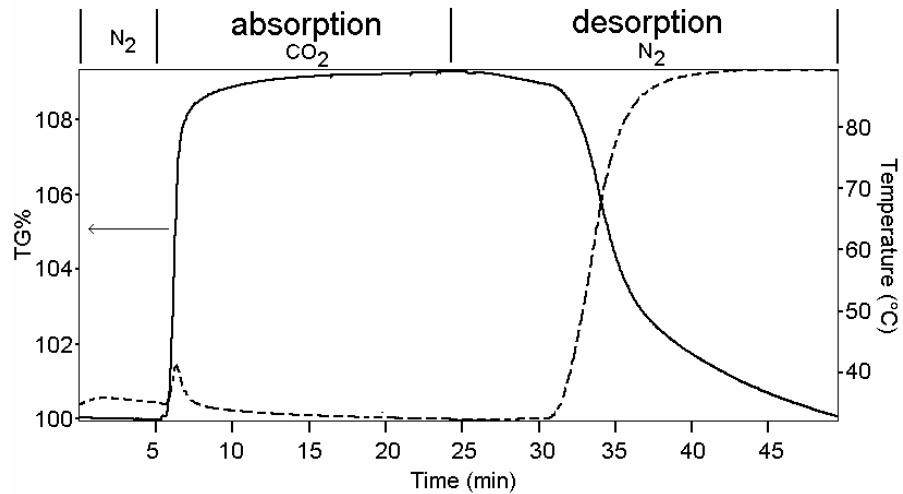
TABLE 2: CO<sub>2</sub> CAPTURE PERFORMANCE OF THE SORBENTS

Sorbent code	Sorbent	Amine loading (% w/w)	CO <sub>2</sub> loading (% w/w)
A1-N1	Sorb-09	47.5	8.7
A2-N1	Sorb-26	24.1	4.15
A3-N1	Sorb-28	37.3	6.08
A4-N1	Sorb-29	27.2	4.12
A1-N2	Sorb-33	40.6	7.8
A1-N3	Sorb-46	33.7	7.65
A1-N4	Sorb-48	44.2	7.9
A1-N5	Sorb-51	44.1	6.46
A1-(N1+N3)	Sorb-49	49.8	9.6

As a final evaluation of the experimental results, sorbent Sorb-09 gave the best performance (8.7 % of captured CO<sub>2</sub>) and good reliability (16 repeated cycles with minor loss in efficiency). A further improvement was achieved by the mixing of two amines (N1 + N3), obtaining a new sorbent (Sorb-49) with the highest overall capture performance (9.6 %).

A typical TG experiment of CO<sub>2</sub> absorption/desorption with sorbent Sorb-09 is shown in Figure. 1.

FIG. 1: CO<sub>2</sub> ABSORPTION/DESORPTION CYCLE ON SORB-09 BY TGA



## PROCESS SIMULATION

### Preliminary process design

A preliminary process design was developed with the aim of assessing the potential industrial use of the selected solid sorbent (Sorb-09). This process consists of several trains of absorbing beds working on Temperature Swing Adsorption (TSA) cycles. The main unit of this scheme, shown in Figure 2, is made of two columns: the first one is working on the absorption mode, while the other is in the regenerative phase. The flue gas is fed to the absorption column through the blower after refrigeration in the cooling water heat exchanger. CO<sub>2</sub> is captured by the solid sorbent at the temperature of about 40 °C, while the decarbonated gas leaving the absorber is supplied to the stack. The regenerative phase is operated in two steps: at first the exhaust bed is heated by recirculating the same gas through the blower and the LP steam heat exchanger. In this phase, as the temperature rises,

the CO<sub>2</sub> is released and the excess is removed through the pneumatic valve. When the bed achieves the temperature of 90 °C, we assume that the release of CO<sub>2</sub> is concluded. After, the bed is cooled to the absorption temperature of 40 °C, by blowing fresh air into the column and a new cycle can start. In order to keep the air temperature entering the bed at about 35 °C, a refrigeration is necessary after the blower.

The preliminary process design was performed by the aid of a specifically developed model that allowed the simulation of the absorption phases and the heating/cooling cycles. The model parameters of the absorption stage were obtained from the regression of a breakthrough curve got from the pilot apparatus and referred to a stream of 300 ml/min synthetic flue gas fed in a bed containing granular Sorb-09. For the process modelling a conservative value of the sorbent CO<sub>2</sub> uptake (6.8 instead of 8.7 % w/w) was adopted.

The process was compared to the conventional technology based on MEA absorption, shown in the Figure 3, which has been demonstrated in many plants, with different purposes, at a bwer capacity [9,10]. The modelling of the MEA absorption process was carried out using the PRO/II® process simulation program [11]. The common base of the comparison was the flue gas from a 465 MWe combined cycle power plant with a 3.4 % CO<sub>2</sub> content.

Both the processes were modelled at the same plant capacity of 4000 ton/d of CO<sub>2</sub> recovered, with an average removal efficiency of 90%. Additional constrains, limiting: the bed diameter, the gas superficial velocity and the pressure drop, were added to the solid sorbent based process in order to limit the capital investment and the energy consumption. The process modelling results, summarized in Table 3, show a large electric consumption for the solid sorbent process. At the equipment level, this is due to the blower duties that in the case of solid sorbents are needed in double amount, for the absorption and desorption steps caused by the higher pressure drop inside the beds.

TABLE 3: PROCESS MODELLING

	Amine	Solid Sorbent
Raw material		
MEA or Sorbent (ton/h)	0.25	0.5
Process water (ton/h)	104	-
Utilities		
Cooling Water (ton/h)	17200	11250
L. P. Steam (ton/h)	360	24
Electric Energy (Mwh)	15	101

On the other hand the steam requirement is higher for the conventional process. This steam, employed in the reboiler of the regenerative column, has an electric equivalent of about 48 Mw if expanded in a turbine at 0.08 kg/cm<sup>2</sup>.

The major equipment size estimates have shown that 40 solid beds (20 in the regeneration phase) of 10 m diameter and 4 m height are needed for the solid sorbent process, while the conventional process requires 2 absorber and one stripper respectively of 10.5 and 7.2 m diameter.

The discrepancy in the number of columns estimated for the two processes depends on the different superficial gas velocities. In the case of the solid beds, the superficial gas velocity is limited by the pressure drop, which must be low to avoid high power consumption. The above requisite is particularly important if operating at low pressure because the pressure drop has a great impact on the compression ratio of the blowers and then on the compression work. In the case of the liquid amine absorption columns, whose superficial gas velocity limitation is given by flooding, the superficial gas velocity is about an order of magnitude greater then with the solid beds, assuming the use of structured packing,

### Sensitivity analysis

After the preliminary process design a sensitivity analysis has been carried out in order to explore the potential of plausible technological improvements. We evaluated the possible advantages coming from the following improvements:

- ? reduction of the regeneration temperature from 90° to 70°C;
- ? 50% increase in the specific CO<sub>2</sub> capture activity of the sorbent (from 6.8% to 10.2%, by mass);
- ? use, under different superficial gas velocities, of a structured monolith support of 1.8 mm pitch instead of the original 2-3 mm pellet shaped one, used in the experimental apparatus;
- ? combination of the two best previous results assuming to employ both the monolith support and the 50% increase in the specific CO<sub>2</sub> capture.

TABLE 4: SENSITIVITY ANALYSIS

	Base case	Regen. Temp. 70 °C	+50% Increased Capture	Monolith	Monolith double velocity	Monolith Capture +50%
Cycle time (h)	3.2	3.2	4.8	1.5	1.5	2.4
Number of beds	40	40	40	40	20	40
Bed diameter (m)	10	10	10	10	10	10
Bed height (m)	4	4	4	4	8	4
Superficial gas velocity (m/s)	0.5	0.5	0.5	0.5	1.0	0.5
Utilities						
Cooling Water (ton/h)	11250	10990	6360	13090	19220	8040
L. P. Steam (ton/h)	24	-	24	40	25	27
Electric Energy (Mwh)	101	100	71	69	116	53

Some of the main results shown in Table 4 are summarized below.

- ? The reduction of 20 °C of the regeneration temperature involves a decrease in the heat duty for the beds heating. In this case the heat transfer by the blowers is sufficient to perform the heating without extra steam.
- ? The increase in the specific CO<sub>2</sub> capture affects the cycle's length, that means more time to complete the beds heating/cooling phases, which may be performed with lower flow rates. In this case smaller blowers may be employed, in the regeneration phase, with a less energy consumption.
- ? The use of a structured monolith support, under the same operative conditions of the base case, implies less pressure drop. However, the lower density of the sorbent forces to cut the cycle time, if the same beds dimensions are used. In the absorption phase a gain is obtained because the blowers power requirement decreases, instead in the regeneration phase we deal with two opposing effects: the decrease of the regeneration time forces to operate with higher flow rates, in order to complete the heating/cooling phases, while the increased permeability of the sorbent allows to operate with less pressure drop. The consequence is a lower power consumption by the blowers, but a higher steam demand in the heating.
- ? It is possible to reduce the number of the beds needed, operating with the monolith support at a double superficial gas velocity, however, in order to compensate part of the time cycle reduction it is necessary to increase the beds height, with an increase in the pressure drop. During the regeneration the reduction of the cycle time forces to operate with higher flow rates increasing the energy requirement.

- ? A more favourable case is established by combining a monolith support with a 50% increase in the capture capacity. In this case the cycle duration is long enough to allow lower flow rates during the regeneration phase. The gain concerns both the absorption and regeneration phases, because smaller blowers are needed.

FIG.2: SOLID SORBENT PROCESS SCHEME

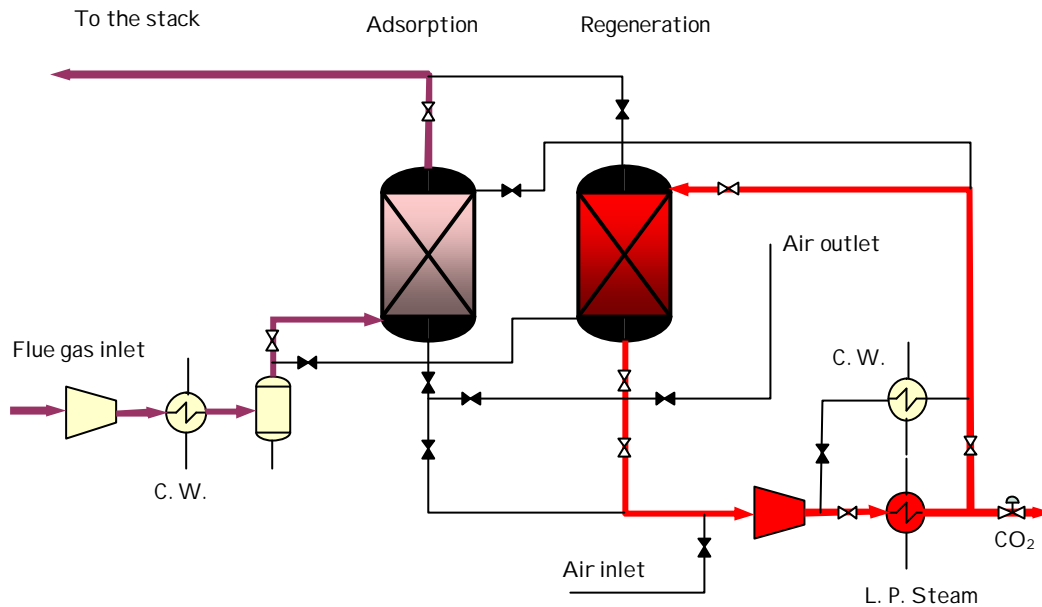
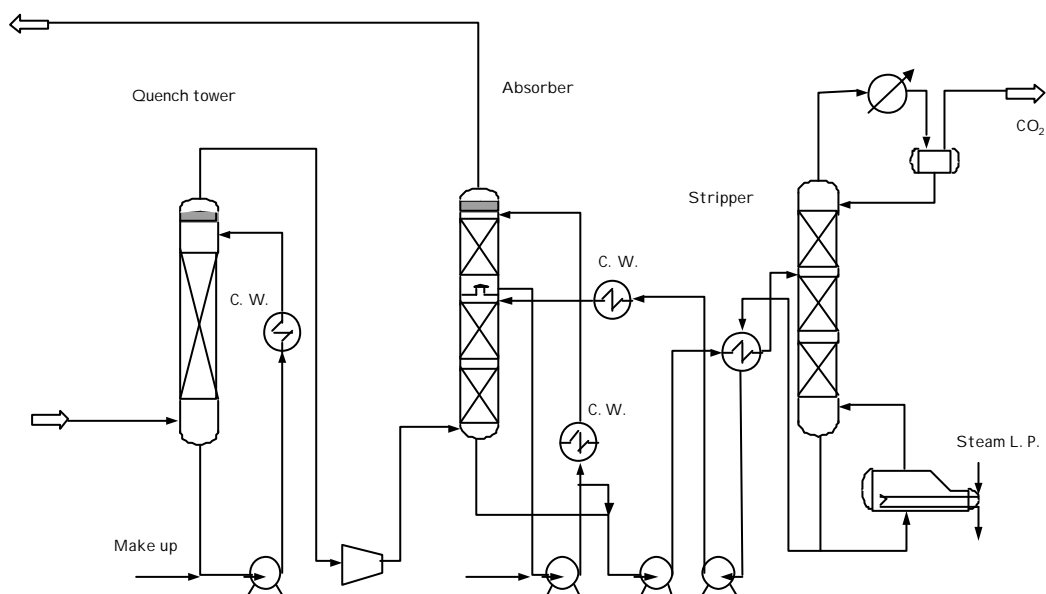


FIG 3: CONVENTIONAL LIQUID AMINE PROCESS SCHEME



## ECONOMIC EVALUATION

All of the cases shown in Table 4 were evaluated by the economic point of view. The “best” case was found to be the last one, which makes use of a structured monolith support, and assumes a 50% increase in the specific CO<sub>2</sub> capture vs. the “base” case. The best case was compared with a conventional amine process. It has to be noted that the comparison didn’t take into account the cost of compression, transport and disposal of removed CO<sub>2</sub>, which both plants deliver to plant battery-limits at near-atmospheric pressure.

In the comparison, reference was made to an industrial application for the removal of 90% of CO<sub>2</sub> from the flue gas of an existing GTCC power station.

The main characteristics of the production plant are shown in Table 5.

TABLE 5

<b>Base Power Station</b>	
GTCC	465 MW
	3720 GWh/year
efficiency	51.4 % (LHV)
natural gas feed	
mol. weight	20.05
LHV	47.6 MJ/kg
CO <sub>2</sub> emission	405.7 kg/MWh
specific investment	550 US\$/kW
(including ancillaries, start-up, pre-prod.)	

Table 6 shows the calculated transfer price of the electricity produced in the base power plant, without CO<sub>2</sub> abatement. This transfer price has been assumed as the price of the power consumed by the removal processes, and has been used as well as a basis for the price of consumed steam (134 kWh of electricity / ton of steam).

TABLE 6

<b>Electric Energy Transfer Price</b>	
	\$/MWh
natural gas (3.5 \$/mill.btu HHV)	25.65
labor & maint. (4% inv.)	2.01
overheads, insurance	1.74
capital charges	
(8% interest rate, 15 years)	9.08
total transfer price	38.48

The estimated energy consumption of the two processes is reported in Table 7. The solid sorbent process requires more electric energy, mainly due to the compressors needed for the desorption phase, while the amine process requires more steam, used in the stripping tower to recover the amine solution. The overall energy balance is in favour of the solid sorbent process.

TABLE 7

<b>Energy Consumption, GWh/year</b>		
	<b>solid sorb.</b>	<b>amine</b>
steam	29.0	384.8
electric energy	421.6	122.4
total	450.6	507.2
power plant derating	12.1%	13.6%

The investment cost was estimated to be about US\$ 278 million for the solid sorbent process and about US\$ 172 million for the amine process. These figures do include allowances for start-up and pre-production (5%) and for interconnecting with the power station (10%). They include interests during plant construction, based on 3 years construction and 8% interest rate, as well.

The above estimates were carried out by the help of a commercial software [12], starting from the main equipment data sheets. Given the preliminary level of the process design and the large number of assumptions, the accuracy of the estimates is supposed to be within the range +/-30%.

It has to be said that the investment cost of the solid sorbent process does not include the cost of the sorbent material. This is due to the fact that so far the actual cost is not known, being the support an experimental compound. On the other hand, the main purpose of the evaluation was to get a rough assessment of the potential of solid sorbent technology, in order to single out possible R&D objectives.

Based on the above data, the cost of CO<sub>2</sub> capture was calculated as reported in Table 8. The CO<sub>2</sub> removal cost with solid sorbents is about 5 US\$/ton (12.6%) higher than the cost with amines.

TABLE 8

<b>CO<sub>2</sub> Capture Cost (US\$/ton CO<sub>2</sub>)</b>		
	<b>solid sorb.</b>	<b>amine</b>
variable cost	13.7	21.0
labor & maint.	5.1	3.3
other fixed	4.0	2.6
capital charges	24.6	15.2
(8% interest rate, 15 years)		
total capture cost	47.4	42.1

In addition to the CO<sub>2</sub> removal cost, the two technologies were compared by estimating the cost of *avoided* CO<sub>2</sub>.

As it is well-known, this is a way to take into account the CO<sub>2</sub> emission (*indirect CO<sub>2</sub>*) associated with the production of the energy consumed by the removal process:

$$\text{CO}_2 \text{ avoided} = \text{CO}_2 \text{ captured} - \text{indirect CO}_2 \text{ emission}$$

There are, in principle, a number of possible ways and assumptions to calculate the cost of avoided CO<sub>2</sub>. We have chosen the following equation proposed by EPRI/DOE. The numerator is the difference between the specific costs of electric energy, with and without capture; the denominator is



<b>EPRI / DOE Equation for Avoided CO<sub>2</sub> Cost</b>	
\$/ton =	$\frac{(\$ / \text{MWh})_{\text{with\_capture}} - (\$ / \text{MWh})_{\text{without\_capture}}}{(\text{ton CO}_2 / \text{MWh})_{\text{without\_capture}} - (\text{ton CO}_2 / \text{MWh})_{\text{with\_capture}}}$

the difference between the specific emissions of CO<sub>2</sub> from the power station, before and after CO<sub>2</sub> capture.

The parameters needed for the formula have been derived from the data of the base power station and removal technologies previously reported. The results are shown in Table 9.

TABLE 9

Cost of Avoided CO <sub>2</sub>				
		without capture	with capture	
			solid sorb.	amine
electric energy	GWh/year	3720	3269	3213
	\$/MWh	38.5	58.2	56.3
CO <sub>2</sub> emission	k ton/year	1509	151	151
	kg/MWh	405.7	46.2	47.0
Cost of avoided CO <sub>2</sub> \$/ton			<b>54.8</b>	<b>49.6</b>

It can be seen in Table 7 that the power station derating is lower for solid sorbent process than for amine. That is, with the capture plant running and consuming energy, the net electricity production (i.e. the electricity sold to the market) with solid sorbent is higher than with amine (see Table 9). In order to understand whether this fact could influence the comparison, a case was studied with the same net production of electric energy. The assumption was to buy on the market the energy needed by the capture process, so allowing the power station to keep its full production (3720 GWh/year). In this purpose, it was supposed to purchase the electricity from a facility similar to the base power station of Tables 5 and 6 (price 38.5 \$/MWh) with associated CO<sub>2</sub> emission of 405.7 kg/MWh.

In this way, and applying the EPRI/DOE equation, different figures were calculated for the cost of electricity and the specific CO<sub>2</sub> emission after capture, but the cost of avoided CO<sub>2</sub> was exactly the same as above: 54.8 \$/ton for the solid sorbent and 49.6 \$/ton for the amine process.

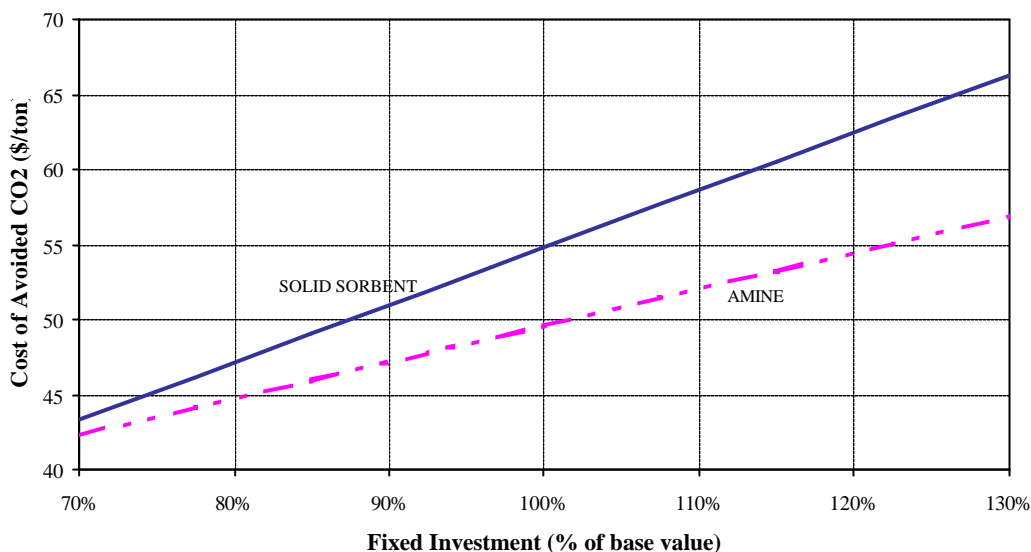
In conclusion, the difference between the two processes in terms of avoided CO<sub>2</sub> is substantially the same as it is in terms of capture cost: in our opinion, such a result should not be seen as a general rule, but perhaps as a consequence of the fact that the difference between the energy consumption of the two processes is rather small.

The higher cost of the solid sorbent process is largely due to the investment cost. Given the obvious uncertainty of estimates, it's interesting to figure out how that does influence the comparison.

It can be seen from the graph (Fig. 4) that the two processes have the same cost for the avoided CO<sub>2</sub> when: first, the amine investment is at base value (100%) and the sorbent investment is at 87% (in this case the cost of avoided CO<sub>2</sub> is about 50 US\$/ton); second, the sorbent investment is at base value (100%) and the amine investment is at 120% (in which case the cost is about 55 \$/ton).

FIGURE 4

### SENSITIVITY to INVESTMENT COST



In both cases, the two processes show the same cost of avoided CO<sub>2</sub> as a consequence of changes of investment cost which are inside the range of accuracy of estimates (+/-30%).

## CONCLUSIONS

The wide range of solid sorbents prepared and their testing for the reversible CO<sub>2</sub> capture, has allowed to draw the following conclusions:

- ✍ High performance materials for CO<sub>2</sub> capture have been prepared by the proposed method of inorganic support impregnation with amines. In particular, an alumina support A1 and the alkanolamines DEA and BIEEDA allowed to obtain a material with a CO<sub>2</sub> uptake activity close to 10% by sorbent weight.
- ✍ Technical economic considerations indicate the applicability of this approach, provided further development is carried out, in order to reach the competitiveness with the current liquid amine technology.
- ✍ The difference between the proposed solid sorbent process and the conventional liquid amine one, in terms of avoided CO<sub>2</sub> is substantially the same as it is in terms of capture cost. Such a result should not be seen as a general rule, but perhaps as a consequence of the fact that the difference between the energy consumption of the two processes is rather small.

## REFERENCES

1. Hattenbach, R.P., Wilson, M., Brown, K.R. (1999) in: *Greenhouse Gas Control Technologies*, pp. 217-221, Riemer, P., Eliasson, B. and Wokaun, A. (Eds). Elsevier, Oxford
2. Moritis, G. (2001) *Oil & Gas Journal* **99**(20), 68.
3. Zappelli, P., Riocci, M., Del Piero, G. and Contarini, S. Ital. Pat. Appl. MI2002A, N° 000536 (EniTecnologie, Italy)

4. Contarini, S., Barbini, M., Del Piero, G., Gambarotta, E., Mazzamurro, G., Riocci, M., Zappelli, P. (2002) IEA GHGT-6 Conference Proceedings (Kyoto, October 1-4) (In Press).
5. Satyapal S., Filburn, T., Michels, H.H. and Graf, J. (1999) in: *Greenhouse Gas Control Technologies*, pp. 113-118, Riemer, P., Eliasson, B. and Wokaun, A. (Eds). Elsevier, Oxford.
6. Satyapal, S., Filburn, T., Trela, J., Strange, J. (2001) *Energy Fuels* **15**(2), 250.
7. JP 62041709; 23.02.1987 (Mitsubishi Heavy Ind. Co. Ltd., Japan)
8. Kohl, A.L., Nielsen, R.B. (1997) in: *Gas Purification*, 5<sup>th</sup> edition, pp. 42-48, Gulf Publishing Co., Houston, TX.
9. Dan G. Chapel, Carl L. Mariz, "Recovery of CO<sub>2</sub> from Flue Gases: Commercial Trends", Canadian Society of Chemical Engineers annual meeting, October 4-6, 1999, Saskatoon, Saskatchewan, Canada.
10. A Sinclair, "Flue-Gas CO<sub>2</sub> Recovery at Prosint", 593W/029/0/IMTOF, Syntex (www.syntex.com/methanol/pdfs/papers/imtof99-paper8(593w).pdf).
11. PRO/II<sup>®</sup>, Simulation Sciences Inc., 601 Valencia Ave Suite Brea California 92823-6346 USA (<http://www.simsci.com>)
12. AspenTech Icarus Process Evaluator